

## Thermal Energy of Mixtures II

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We have found that conservation of Internal Energy, hence upholding the first law of thermodynamics, obliges us to include configurational entropy in Internal Energy.

We recall:

$$U = U_{\text{mic}} - TS_{\text{conf}} \quad (\text{generally } U = U_{\text{mic}} - \int dTS_{\text{conf}}(T) )$$

$U_{\text{mic}}$  is the microscopic Internal Energy,  $S_{\text{conf}}$  is the configurational entropy of the mixture.  
Heat capacity becomes

$$C_V = C_{V\text{mic}} - S_{\text{conf}}$$

For pure substances,  $S_{\text{conf}} = 0$  and there is no contribution.

How come we got the right result in osmosis without this modification of Internal Energy?

In osmosis, the pressure difference was obtained by equating water chemical potential on each side of a semi-permeable membrane. If, however, we plug our new expression for Internal Energy in, we somehow "double up" the entropy effect arriving at a glaring contradiction.

The reason is that our original reasoning was wrong.

Change of Gibbs potential is

$$dG = -SdT + Vdp = \mu_j dN_j$$

There is a pressure change across the semi-permeable membrane (spm) which I forgot to take into account. When we apply the usual reasoning of (water) particles going to and fro across the spm, the change becomes

$$\Delta\mu_w dN = v_w \Delta p dN$$

This cancels the pressure term in the expression for the chemical potential, leaving us with the (water) molar free energy.

$$\Delta f = \Delta u - T\Delta s = 0$$

This directly gives us the modification of Internal Energy.

An experimental test of the hypothesis exposed would be the measurement of specific heat as a function of configurational entropy, species concentration that is to say, under conditions excluding any parasitic effects. We have such conditions when mixing *isotopes* of one single species.

Practically, take molten metal of two isotopes and measure specific heat vs isotope proportion.  
Choose isotopes of same nuclear spin to avoid quantum statistical issues.

We should get a minimum of specific heat at equal isotope content.

Now that we are done with the nitty-gritty, let us point out that in this year 2024AD, after 200 years of thermodynamics and 150 years of Boltzmann's definition of entropy, we have, on top of kinetic and interaction energy, discovered a new, third, form of energy - *configurational energy*.